Environmentally friendly methods of cellulose production by wood organosolvent pulping

B.N. Kuznetsov*[a], S.A. Kuznetsova[a], V.G. Danilov[a], O.V. Yatsenkova[a], N.B. Alexandrova[b], N.V. Lazareva[a]
[a]Institute of Chemistry and Chemical Technology SB RAS, Akademgorodok, 660036, Russia
Fax: +7(3912)439342; bnk@krsk.infotel.ru, inm@krsk.infotel.ru
[b]Krasnoyarsk State University, Russia

Introduction

Organosolvent pulping is considered as a new promising way of cellulose production [1]. The main advantages of wood delignification in organic medium as compared to conventional pulping process in water solutions are connected with easy recycle of organic solvent and with complete utilization of lignin and hemicelluloses based side-products. Acetic acid and low-molecular-mass alcohols were used as organic solvents. The method of oxidative delignification f wood with peracetic acid, which is formed in *situ* in the pulping liquor at proper ratio of acetic acid/H_2O_2 is of apparent interest, becouse under these conditions the selective oxidation of lignin units has been observed [2].
Goal of the present work is to optimize the process of silver-fir, aspen and pine wood delignification with organic solvent in the presence of oxidizing reagents and catalytic additives. The obtained experimental data describe the influence of H_2O_2, catalysts (H_2SO_4, HCl, TiO_2, $TiCl_3$, $NaMnO_4$, $Fe(OH)_3$, ZnO, Cr_2O_3), operating parameters of organisolvent pulping process on the yield and characteristics of produced cellulose.

Experimental

Wood chips (silver-fir, aspen, pine-wood) with size 20×11×0.5 mm were used in pulping experiments. Methanol, butanol-1 and acetic acid were used as organic solvents. Hydrogen peroxide (35%) was used in combination with acetic acid (30%) with the mole ratio H_2O_2/CH_3COOH variation in the range 0.1-0.9. Sulphuric acid with concentration 1-2.5% on a.d.w. and other catalysts (TiO_2, $NaMnO_4$ etc.) with concentration 2% on a.d.w. were used for promotion of delignification process.
The pulping process of wood was studied in a static reactor with volume 200 cm^3 at the temperatures 120-150^oC, during 1-5 hours. The cellulosic material obtained was analyzed according to standard methods.

Results and discussion

The process of aspen and pine-woods delignification by methanol at 200^oC yields lignocellulosic product with decreased content of lignin and hemicelluloses. The addition to reacton medium 5% HCl increases the concentration of cellulose (to 81-82% wt.) and decreases the amounts of lignin (to 7-10 % wt.) and hemicelluloses (to 9-10% wt.) in obtained lignicellulosic product. Besides, the cellulose content was increased with the growth of time of wood treatment by pulping liquor from 5 to 10 hours. The promotion effect of $Fe(OH)_3$ additive was observed in the process of aspen-wood delignification by butanol-1 (cellulose concentration in lignocellulosic products was reached to 86% wt.).
The process of silver-fir wood delignification in acetic acid solutions with addition of H_2O_2 was optimized on pulping liquor composition, sulphuric-acid catalyst concentration, temperature and process time. It has been found that at moderate temperatures (to 95^oC) the addition of H_2O_2 to acetic acid solution increased the content of cellulose without significant decrease of lignocellulosic product yield. The higher temperatures (120-130^oC) promote the reactions of lignin oxidative destruction resulting in the increase of cellulose content (to 71.9% wt.) in obtained product. But both the yield of lignicellulosic product and cellulose content were decreased at pulping temperatures 140-150^oC and longer times of treatment as a result of oxidative destruction of lignin, hemicellulose and amorphous part of cellulose. Obtained results show that temperature 130^oC and pulping process time 3h supply the high content of cellulose at optimum yield of lignocellulosic product (55.2% wt.).

Sulphuric acid promotes the wood delignification in H_2O_2/CH_3COOH solutions. The optimum concentration of H_2SO_4 catalyst in pulping liquor resulting in the highest content of cellulose in lignocellulosic product (71.9% wt.) was defined as 2% wt. on a.d.w. The higher concentrations of

H_2SO_4 decrease the yield of lignocellulosic product. At the lower concentrations of catalyst the obtained product has high content of lignin.

Delignification properties of pulping liquor with composition: acetic acid+H_2O_2+sulphuric acid can be improved by optimizing the H_2O_2/CH_3COOH ratio due to the formation of a certain amount of peracetic acid. The latter promotes a deeper oxidation of lignin resulting in a higher degree of wood delignification. It has been found that the optimum mole ratio H_2O_2/CH_3COOH corresponding to rather high yield of product (55% wt.) with significant amount of cellulose (71.9% wt.) was around 0.3. At higher ratios the lower yield of product with decreased lignin content was observed (for example, at mole ratio 0.7 the yield of product was 31.7% wt. and lignin content 3.3% wt.) At low H_2O_2/CH_3COOH ratio (0.1) the yield of product and lignin content were 64.5 and 31.1% wt. respectively.

The rate of organosolvent pulping is limited by diffusion phenomena At low liquor/wood ratio [3]. Obtained data show that at high liquor/wood ratio (15:1 and 20:1) the diffusion processes are accelerating. This results in producing of cellulosic product with content of lignin as low as 5.7 and 0.7% wt. and cellulose – 80.5 and 85.4% wt. accordingly at time of pulping 3 hours. At high liquor/wood ratio (20:1) the time of delignification treatment can be cut down up to 2 hours. At these conditions the cellulosic product containing 85.6% wt. cellulose and 7.9% wt. lignin was produced with yield 56.4% wt.

The most pronounced catalytic effects should correspond to conditions of wood delignification in the absence of diffusion limitations. It means that the significant influence of catalyst on the pulping process have to be expected at high liquor/wood ratios. Data on the silver-fir wood catalytic delignification at liquor ratio 20:1 are supported this assumption. The positive effect of catalyst on the wood delignification process was observed for H_2SO_4 and TiO_2 after 2 hours, and for Na_2MoO_4 – after 1 hour. The degree of lignin removing during wood delignification was increased from 50,5 % (without catalyst) up to 83,9 % in the presence of sulphuric acid catalyst.

The positive action of sulphuric acid catalyst was observed also in the two-step delignification process. The first step of this process includes the wood impregnation at liquor/wood ratio 15:1. This step provides soft selective oxidation of lignin and polyoses unites and promotes the removal of extracted compounds and oxidized products from wood. After replacement of impregnating liquor on pulping one it is possible to carry out the second step with lower liquor ratio (10:1). This makes it possible to decrease the lignin content in product to cut down the process time and to obtain cellulosic material with 81,8% cellulose and 7,7% lignin.

Two step organosolvent pulping makes possible to produce pure microcrystalline cellulose for different fields of application (food and polymeric industry, medicine, cosmetics etc.)

References

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